

Analysis of organic compounds in ambient aerosols collected with the particle-into-liquid sampler

Jevgeni Parshintsev¹⁾, Riikka Räsänen¹⁾, Kari Hartonen¹⁾, Markku Kulmala²⁾ and Marja-Liisa Riekkola¹⁾

¹⁾ Laboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55, FI-00014 University of Helsinki, Finland

²⁾ Division of Atmospheric Sciences, Department of Physics, P.O. Box 64, FI-00014, University of Helsinki, Finland

Received 21 July 2008, accepted 17 Nov. 2008 (Editor in charge of this article: Veli-Matti Kerminen)

Parshintsev, J., Räsänen, R., Hartonen, K., Kulmala, M. & Riekkola, M.-L. 2009: Analysis of organic compounds in ambient aerosols collected with the particle-into-liquid sampler. *Boreal Env. Res.* 14: 630–640.

A particle-into-liquid sampler (PILS) was applied to the collection of atmospheric aerosol particles for the analysis of α -pinene and its oxidation products. A cyclone and four denuders were coupled to the PILS to eliminate large particles and minimize the negative effects of gas-phase compounds. The PILS setup, sampling time, number and quality of denuders, sample pretreatment and analysis were optimized. Pinonaldehyde, α -pinene, pinic acid and *cis*-pinonic acid were selected for the investigation. The results showed that the PILS is suitable for the sampling of biogenic aerosols because oxidation, evaporation and adsorption, which are the most important sources for artifacts in filter and impactor sampling, can be minimized. In addition, a short sampling time and capability for on-line analysis of major organic compounds in aerosols make this a promising technique for obtaining reliable information about particle composition with the good time resolution. In addition, the PILS can be on-line coupled to mass spectrometry. Advantages and disadvantages of the PILS in regard to the analysis of organic compounds are discussed.

Introduction

Aerosol particles contribute significantly to the Earth's radiative budget and to climate change (Kulmala *et al.* 2004, Lohmann *et al.* 2005, Spracklen *et al.* 2006). It is important, therefore, to understand the processes taking place during the growth of atmospheric aerosols and the lifetime of the particles. Qualitative and quantitative information about compounds in aerosol particles needs to be available if we are to comprehend the role and effects of aerosol particles in the atmo-

sphere. Qualitative chemical information about aerosols can be obtained on-line by various mass spectrometric techniques (Drewnick *et al.* 2005, Allan *et al.* 2006), but quantitative information is still rare. Off-line methods, which typically include sample collection on filters or impactors, can be employed for conventional analysis. Unfortunately, however, these sample collection techniques suffer from sampling artifacts. For example, if not removed, tropospheric ozone will oxidize unsaturated compounds during a long sampling period (Liu *et al.* 2006). Absorp-

tion of gaseous semivolatile organic compounds onto the filter and their evaporation from it are potential sources of measurement error (Mader *et al.* 2001). In addition, the time resolution of off-line sampling techniques tends to be unsatisfactory, even where diurnal variations of the most dominant species are being measured. Aerosol size separation before or during the sampling can be achieved by impactor and other techniques, but the collection time needed for an analysis of even total organic carbon is at least 24 h (Viidanoja *et al.* 2002). Filter sampling is usually done without size separation (Rissanen *et al.* 2006), though recently virtual impactors have been applied to cut off the largest particles in filter sampling (Sillanpää *et al.* 2006).

Clearly, there is a need for new and more precise sampling techniques that are less sensitive to artifacts and provide better time resolution, and can even be coupled on-line with a detection technique. The particle-into-liquid sampler (PILS) was introduced by Weber *et al.* (2001). Later, the device was improved for ground and airborne measurements of water-soluble-aerosol composition (Orsini *et al.* 2003). The PILS combines two conventional techniques in aerosol measurement: particle growth in oversaturated water vapor and impaction on a quartz impactor. For the determination of aerosol inorganic ion composition, particles are flushed with pure water to a debubbler, which removes air bubbles in a T-shaped fitting by weak suction on one leg, and then introduced to an ion chromatograph. The liquid flows are controlled by an eight channel peristaltic pump, while the liquid flow rate in each channel is determined by the inner diameter of the tubing. Sample air is introduced to the PILS by a vacuum pump, and air flow of $1 \text{ m}^3 \text{ h}^{-1}$ is controlled by a critical orifice. Originally, the PILS was coupled with two ion chromatographs for separate anion and cation analysis. Also, total organic carbon has been measured, after filtering of the PILS sample, on-line with a total organic carbon analyzer. A detection limit of $1 \mu\text{g C m}^{-3}$ was achieved (Sullivan *et al.* 2006, Kondo *et al.* 2007). Although several interesting and important studies have been performed with PILS, it has not been applied to the analysis of individual biogenic organic compounds. That was the task of our work.

The PILS was of particular interest for our research due with no air flow through the sample, it is less sensitive to artifacts caused by evaporation and absorption. Furthermore, with the set up we employed, ozone and organic gas-phase compounds can be removed, which prevents the oxidation of compounds and minimizes the adsorption of low volatile species. In addition, the oxidation by hydroxyl radicals should not be a problem as these will not survive transport through the relatively long sampling line.

We studied the applicability of PILS to the collection of organic compounds in aerosol samples. The collection time, sample solvent, the number and quality of denuders, and GC-MS analysis of samples for the selected organic compounds were optimized to obtain the most reliable results. A study was also made of the possibility to couple PILS on-line with electrospray ionization (ESI) mass spectrometry.

Experimental methods

Chemicals and materials

(-)- α -pinene ($\geq 99\%$, GC, sum of enantiomers) was purchased from Fluka Chemie GmbH (Buchs, Switzerland). Internal standards 1,1'-binaphthyl (98%) was from Acros Organics (Geel, Belgium) and decafluorobenzophenone (98%) was purchased from Aldrich (Sigma-Aldrich Chemie GmbH, Steinheim, Germany). Pinonaldehyde was synthesized in the laboratory by oxidation of (1S,2S,3R,5S)-(+)-pinanediol (Aldrich, Steinheim, Germany) with periodic acid (Merck, Darmstadt, Germany) as explained in Glasius *et al.* (1997). *Cis*-pinonic acid (98%) and pinic acid (library of rare chemicals, no purity available) were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Pentafluorobenzyl bromide and 18-crown-6-ether for the derivatization reaction were purchased from Sigma-Aldrich.

Chemicals for the denuder coating were phosphoric acid (85%) and potassium iodide from Merck (Darmstadt, Germany), glycerol from Sigma-Aldrich (Steinheim, Germany), and XAD-2 resin (polystyrene-divinylbenzene) from EGA-Chemie (Steinheim, Germany).

Methanol and dichloromethane were from J.T. Baker (Deventer, The Netherlands). Ethanol (99.5%) was purchased from Altia Corporation (Rajamäki, Finland), *n*-propanol (HPLC grade) from Rathburn Chemicals (Walkerburn, Scotland), and 2-propanol (99.7%) from Labscan analytical sciences (Dublin, Ireland).

Measurement sites

Studies relevant to the optimization of the PILS sampling were carried out in the Laboratory of Analytical Chemistry, University of Helsinki (60°12'N, 24°58'E, ca. 40 m a.s.l., 3rd floor). Air samples were taken through a window of the laboratory, which is located about 6 km north-east of the city center, and about 200 m from a busy traffic artery that feeds to a major motorway.

Samples were collected with the PILS at the Station for Measuring Forest Ecosystem Atmosphere Relations (SMEAR II) at Hyytiälä (61°51'N, 24°17'E, 180 m a.s.l.), which is located 230 km north of Helsinki. The forest consists of Scots pines (*Pinus sylvestris*) 30–40 years old, homogeneously extending 200 m in all directions from the measurement site. A more detailed description of SMEAR II can be found in Kulmala *et al.* (2001).

Instrumentation

The sampling system consisted of an ADI2081 particle-into-liquid sampler (Applikon Analytical, Schiedam, The Netherlands) coupled with an eight channel peristaltic pump (Watson Marlow 205S, Wilmington, USA). Four types of polyvinylchloride tubing were used to obtain the desired water flows in the collector. For the sample, two tubings with an inner diameter (i.d.) of 0.25 mm were used for the flow of 0.16 ml min⁻¹ each. Air bubbles were removed with 0.65 mm i.d. tubing with a suction of 0.30 ml min⁻¹. For the steamer, 1.5 ml min⁻¹ of water was introduced through 1.42-mm i.d. tubing. The carrier water for washing the impactor plate was applied with a flow of 0.30 ml min⁻¹ (0.38 mm i.d.), and steamer waste was removed with two tubing (i.d. 1.85 mm) with a flow of 1.0 ml min⁻¹ each.

Because gas phase compounds may interfere with the aerosol samples during collection and affect the analysis, three channel annular denuders (242 mm length, teflon coated, stainless steel sheath, URG, Chapel Hill, USA) with different coatings were tested for their removal. One denuder was coated with equal parts of solutions of 20 g of potassium iodide in 10 ml of MilliQ water and 10% glycerol in methanol to ensure that the aerosol compounds would not be oxidized during the sampling (Williams *et al.* 1990). The coating was made by decanting the solution into a denuder, shaking the solution and returning it to the beaker. The denuder was then dried with purified air. The same solution can be used many times.

Two denuders were coated with XAD-2 resin. The coating was performed as follows: XAD-2 was ground and purified using Soxhlet with dichloromethane for 24 h. Then the solvent was changed to hexane and the continuously stirred solution was decanted into the weighed denuder, shaken for a while and returned to the beaker. Finally, the denuder was dried with purified air. The procedure was repeated about 10 times until the amount of XAD-2 in the denuder was about 50 mg.

A fourth denuder was coated with phosphoric acid simply by flushing it with 10% phosphoric acid and then dried.

The cyclone (PM2.5, URG, Chapel Hill, USA) used for the size separation of the sampled aerosols was placed before the denuder line, which was connected to the PILS inlet and washed and recoated once a week with the vacuum grease.

Pretreatment of PILS samples

PILS samples (from 10 to 40 ml) were placed in a separation funnel and 10 µl of internal standard was added. Twenty-five drops of 1 M hydrochloric acid (sample pH about 1.5) were added to make the acidic compounds neutral and more soluble in dichloromethane. About 200 mg of sodium chloride was added to the sample to enhance the extraction efficiency. Liquid-liquid extraction (LLE) was done three times with 10 ml of dichloromethane. The organic fraction was separated, dried with sodium sulfate,

and filtered through purified cotton wool. The amount of solvent was reduced to 500 μl with a gentle stream of nitrogen. For the determination of pinic and *cis*-pinonic acids, half of the samples were derivatized with pentafluorobenzyl bromide. First, samples were dried with nitrogen and 1 ml of acetone was added. Anhydrous potassium carbonate (ca. 40 mg) was then added to remove water produced during the reaction. After pentafluorobenzyl bromide solution (90 μl , 10% in acetone) and 370 μl of 16-crown-6-ether were added. The reaction mixture was held at 65 °C for 90 minutes. Derivatized samples were filtered through the syringe filter (0.45 μm pore size) and evaporated to dryness and finally dissolved in 0.5 ml of hexane.

Gas chromatographic-mass spectrometric analysis

Before each analysis, 10 μl of quantitation standard, 1,1'-binaphthyl, was added to the vial. Chromatographic analyses were performed with a gas chromatograph (Agilent 6890N, USA) equipped with a mass selective detector (Agilent 5973N, USA). The GC column was an HP-5 (29 m \times 0.25 mm \times 0.25 μm , Hewlett Packard, USA) coupled with a 2-m deactivated retention gap (i.d. 0.53 mm, Agilent, USA) via a press-fit connector (0.30 to 0.75 mm OD, deactivated; BGB Analytik, Switzerland). The GC oven temperature was programmed as follows: initial temperature 60 °C (2 min), temperature gradient 10 °C min^{-1} with final temperature 300 °C (10 min). 1 μl of sample was injected by on-column injection. The injector temperature program was in track-oven mode. Helium was used as carrier gas with a constant flow of 1 ml min^{-1} . The interface between the GC and the MS was maintained at 300 °C, while the ionization source was kept at 150 °C. Electron impact ionization (EI) was used at 70 eV for monitoring of ions from 50 to 500 amu in nonderivatized samples. Selected ion monitoring (SIM) was employed for the derivatized samples.

Quantitation of target compounds

The GC-MS data was analyzed with the

Enhanced ChemStation D.00.01.27 software (Agilent, USA) and the compounds of interest were identified from aerosol sample chromatograms by their retention times and mass spectra. Quantification was done with a five-point calibration based on the extracted ion chromatograms. Ion 181 from the derivatization agent, which was the most abundant ion, was used for the quantitation of acids. Reference solutions and samples were analyzed three times and the mean peak area values were calculated.

Direct mass spectrometric analysis

To check the feasibility of real-time analysis of organics collected by PILS, samples were analyzed off-line by atmospheric pressure ionization mass spectrometry. Electrospray ionization was used in a Bruker Esquire 3000 plus ion-trap mass spectrometer (Bruker Daltonics Inc., USA). Negative ionization mode was tested. The PILS samples (with 5% of acetonitrile) were introduced to the ionization chamber by syringe pump (350 $\mu\text{l min}^{-1}$). Scan range from 50 to 200 m/z was used in order to see pinic and *cis*-pinonic acids. Other parameters for negative ionization were capillary voltage 3800 V, end plate offset -500 V, nebulizer pressure 2.72 atm, drying gas temperature 320 °C, and flow 8 l min^{-1} . MS/MS experiments were done with ions 183 and 185 to ensure identification of pinic and *cis*-pinonic acids.

Results and discussion

The optimization of the PILS sampling system was done in the laboratory, with locally collected samples. The first step was to determine the efficiency of the denuder for the removal of gas-phase compounds. In theory, gas-phase compounds should be sucked to the vacuum, and only grown aerosols should proceed from the impactor to the sample flow. However, the temperature of water steam is high, which means that reaction rates are high and even a few milliseconds may be sufficient for some compounds to react with aerosol compounds. It is important, therefore, to get rid of as much of the gas-phase

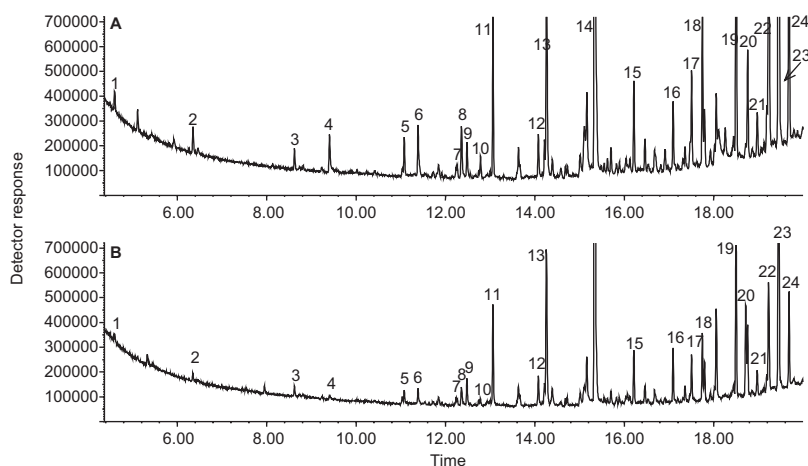


Fig. 1. GC-MS (TIC) chromatograms of PILS samples obtained (A) after teflon filtering and (B) after teflon filtering combined with XAD denuder. Compounds identified by NIST library were (1) dimethyltriazine, (2) ethylhexanol, (3) naphthalenone, 4 benzothiazole, 5,6-derivatives of propanoic acid, 7,14,17,20,21,23-hydrocarbons, 8,9,10-oxidized hydrocarbons, 11-hydroxytoluene, 12,13,16-phthalates, 15-chloromethylbutanone, 18-hexadecanoic acid ester, 22-substituted phenol, 24-octadecanoic acid ester.

compounds as possible. Their removal in the denuder is based on their higher diffusion rates and thus adsorption on the active surface.

Potassium iodide coating was chosen for the removal of ozone because, according to Helmig *et al.* (1995), it does not have to be renewed for at least 63 hours if the flow rate of the sample air is 20 l min⁻¹ and the concentration of ozone is 200 parts per billion (ppb); although some organic compounds may react with such a coating, there is no evidence that the biogenic compounds of interest react in this way. The ozone-removing denuder was easy to prepare, and the coating lasted for five days or longer depending on the ozone concentration in the sampled air (typically about 45 ppb at Hyttälä). Overloading of the coating material was easily determined by a change in color from white to yellow. Removing ozone from the sample air was expected to have a marked effect on the results.

Since some basic gas-phase compounds, ammonia for example, could affect the stability of the sampled compounds and hinder sample pretreatment, we added a phosphoric acid denuder to the denuder line. Although the lifetime of the coating was not determined, it was decided to recoat the denuder once a week.

Organic gas-phase compounds may also cause artifacts during sampling by adsorbing

onto the aerosols during their growth in water steam. A XAD-2-coated denuder was tested for their removal. With a teflon filter inserted in the inlet to remove all aerosols from the air, two one-hour samples were collected with PILS, the first with an XAD coated denuder in the denuder line and the second without an XAD denuder. GC-MS (TIC) chromatograms of the two samples (Fig. 1) revealed that the areas of the numbered peaks are reduced with the use of the XAD denuder, though to a lesser extent than was expected. As quantitation of all the compounds was not reasonable, peak areas rather than concentrations were used for the comparison. Volumes of the samples were kept the same and there were no differences in the sample pretreatment of the two samples. A few peaks (phthalates) could be excluded from the investigation because of their known origin in the sample pretreatment. Because the gas-phase compounds could not be entirely removed, in the experiment with real samples their effect was minimized by using two XAD denuders in series.

The optimization of sampling time needed for the collection of major aerosol components for the GC-MS analysis was done by collecting one-hour sample fractions. Because the concentrations of the compounds were too low for the quantitative GC-MS analysis, the following

Fig. 2. Typical extracted ion chromatogram of a two-hour PILS sample (Hyytiälä, 24 April 2007, collected from 10:30 to 12:30). Peaks and selected ions are (1) β -pinene (m/z 93), (2) benzaldehyde (m/z 77), (3) α -pinene (m/z 93), (4) pinonaldehyde (m/z 83), (5) norpinonaldehyde (m/z 83).

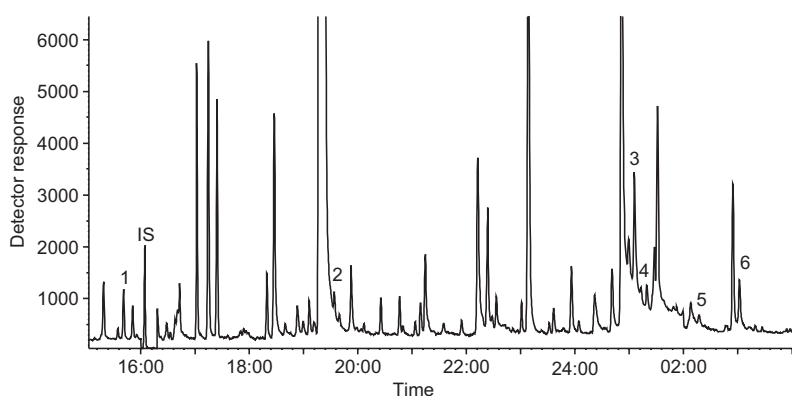
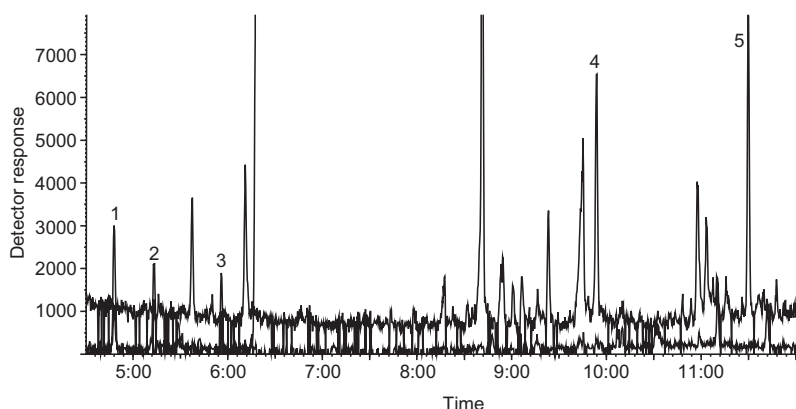


Fig. 3. GC-MS (SIM) chromatogram of a PILS sample collected from 11:00 to 13:00 on 28 April 2007. (1) caprylic acid, IS internal standard; (2) *cis*-pinonic acid; (3) palmitic acid; (4) pinic acid; (5) vanillic acid; (6) stearic acid. SIM ion groups and start times: m/z 83, 181, 324 (5.00 min); m/z 456 (16.00 min); m/z 83, 181 (16.30 min); m/z 69, 181, 255, 436 (24.90 min); m/z 181, 347 (26.00 min); m/z 181, 265 (26.90 min).

three samples were employed: (1) a one-hour sample, (2) the one-hour sample and next one-hour sample combined (same total volume as for the one-hour sample), and (3) sample two combined with the next one-hour sample (same total volume). Because the second sample provided good peak areas for the target compounds, we chose a sampling time of two hours for further work. Samples for the optimization were collected outside of rush hour to eliminate changes in the composition of aerosols. Typical GC-MS (EIC) chromatograms of two-hour PILS samples are presented in Figs. 2 and 3 and the compounds of interest are listed in Table 1.

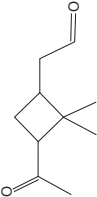
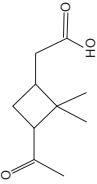
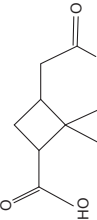
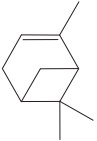
To improve the collection efficiency of less polar compounds, we studied the applicability of alcohols as transport flow solvent. PILS samples were collected during two hours with methanol, ethanol, 1-propanol, and 2-propanol, and the

effect of the alcohols on the samples was studied. Because of the high tip temperature, 90 °C in PILS, solvents were cooled to -20 °C and kept in an ice-bath during the sampling. Also, different speeds of the peristaltic pump were tested in order to obtain the best possible stability of the sample flow.

Measurement of alcohol/water ratios in the PILS samples was carried out using Karl Fischer titration, which is a widely used analytical method for the determination of water content, and by conventional density measurements, where samples were thermostated to 20 °C and the precise volume was weighed. The amount of alcohol was then compared with literature values using the value of density (CRC 1986–1987). Measurements were performed for ten samples of each alcohol, and the mean value was calculated.

A high temperature and low pressure led

Table 1. Structures and nomenclature of the studied compounds.

Compound	Systematic nomenclature	Terpene nomenclature	Structure	MM (g mol ⁻¹)	m/z (EI)
1	3-acetyl-2,2-dimethyl-cyclobutyl-ethanal	pinonaldehyde		168	83 (100) 69 98
2	cis-3-acetyl-2,2-dimethylcyclobutaneacetic acid	cis-pinonic acid		184	181* (100)
3	3-(carboxymethyl)-2,2-dimethylcyclobutanecarboxylic acid	pinic acid		186	181* (100)
4	2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	α-pinene		136	93 (100) 77 121

* ion 181 is from derivatization reagent and is dominant in MS spectra.

to the evaporation of the alcohols before they reached the debubbling cube. Cooling did not prevent the evaporation of methanol, ethanol, or 2-propanol. In the case of 1-propanol, a higher speed 45 rpm of the peristaltic pump was required for sample flow, instead of the 23 rpm used in the case of water. Even though higher pump speed increased sample volumes, it was easier to concentrate the samples collected with 1-propanol. The concentration of 1-propanol in the samples was $88\% \pm 10\%$ by volume. An improved collection efficiency for less polar compounds can then be expected. However, with all alcohols the tubing inside the pump was easily damaged. After 20 hours of use, the PVC tubing began to decompose and no longer provide constant sample flow, and the decomposition products began to contaminate the samples. In view of these problems, water was used as the transport medium in this research.

Four compounds of biogenic origin (Table 1) that are important in atmospheric chemistry were selected for the quantitation of the real samples.

Special attention was paid to pinonaldehyde because of its assumed importance in aerosol growth (Liggio *et al.* 2006, Parshintsev *et al.* 2008). The quantitation was done for the most abundant ions (marked as 100% in Table 1) using extracted MS ion chromatograms.

The amount of *cis*-pinonic acid is much higher than that of the other oxidation products of α -pinene, most probably due to insufficient separation efficiency of GC-MS for an aerosol sample containing hundreds of compounds (Table 2). Because even selected ion monitoring of relatively high masses produced a peak jungle (*see* Fig. 3), interfering compounds likely caused overestimation of the amounts of the studied compounds. Also, *trans*-pinonic acid, which is known to be present in biogenic aerosols in relatively high concentrations, was not separated from *cis*-pinonic acid, presumably due to the GC column employed (Warnke *et al.* 2006). Furthermore, the derivatization procedure, which is different for mono- and dicarboxylic acids, may have altered the real amount of acids. Even the

Table 2. Concentrations (\pm SD) of studied compounds (ng m^{-3}) in sampled air. For the calculation of relative standard deviations $n = 3$.

Sample date (Julian date)	Pinonaldehyde	α -pinene	<i>Cis</i> -pinonic acid	Pinic acid
113.62	57.9 ± 9.4	38.7 ± 6.2	822.6 ± 11.6	30.3 ± 17.7
113.71	39.8 ± 2.8	39.0 ± 6.2	1414.1 ± 4.6	69.8 ± 5.4
114.40	30.7 ± 15.5	60.2 ± 9.6	2527.3 ± 1.4	80.2 ± 7.6
114.48	34.9 ± 12.7	51.7 ± 8.3	1784.5 ± 5.5	140.4 ± 7.7
114.56	52.1 ± 15.7	35.5 ± 5.7	770.9 ± 2.4	11.5 ± 4.9
114.65	34.6 ± 17.3	34.3 ± 5.5	1448.8 ± 8.0	46.7 ± 1.1
114.71	46.9 ± 4.8	34.3 ± 5.4	584.3 ± 9.7	8.3 ± 14.4
115.40	39.2 ± 7.9	51.8 ± 8.3	907.3 ± 8.6	3.5 ± 10.9
115.48	41.0 ± 13.9	51.6 ± 8.2	862.1 ± 29.1	19.9 ± 41.2
115.56	38.9 ± 6.2	50.5 ± 8.0	1104.2 ± 9.6	43.2 ± 1.9
115.65	NA	49.6 ± 7.9	1098.6 ± 9.3	6.2 ± 14.0
115.71	NA	44.3 ± 7.0	807.4 ± 7.3	26.4 ± 4.3
116.40	43.3 ± 20.4	55.4 ± 8.8	2283.4 ± 4.9	69.5 ± 2.2
116.49	36.8 ± 9.9	50.0 ± 8.0	988.3 ± 3.8	82.1 ± 25.2
116.57	35.8 ± 13.5	51.3 ± 8.2	1287.8 ± 2.9	35.2 ± 19.4
116.67	33.4 ± 3.9	51.0 ± 8.1	678.8 ± 14.6	10.4 ± 22.6
117.39*	53.7 ± 17.2	56.8 ± 9.1	$934.2 \pm \text{NA}$	$29.2 \pm \text{NA}$
117.47*	39.4 ± 8.3	51.4 ± 8.2	980.6 ± 10.9	28.9 ± 8.2
117.56*	38.5 ± 5.1	47.7 ± 7.6	806.2 ± 1.2	14.1 ± 8.4
117.66*	29.4 ± 3.2	48.6 ± 7.7	945.9 ± 14.9	18.6 ± 7.9
118.42*	20.1 ± 12.9	57.1 ± 9.1	503.4 ± 3.8	47.6 ± 13.1
118.50*	22.4 ± 20.5	61.2 ± 9.8	1819.7 ± 3.8	5.9 ± 25.3

NA = not available, * = event day samples.

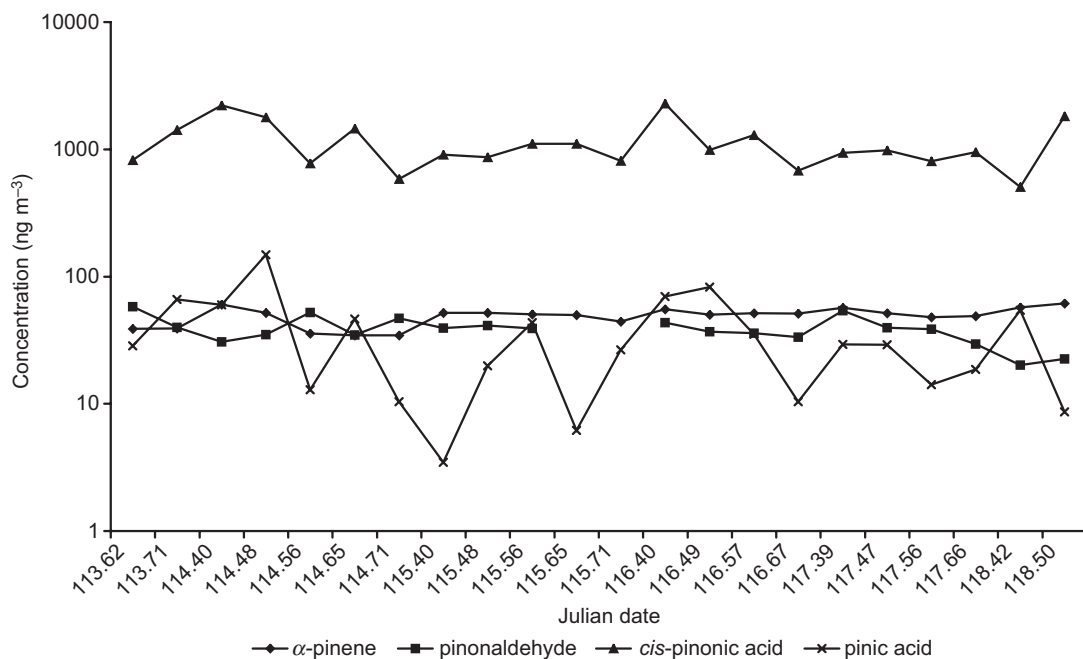


Fig. 4. Concentrations of α -pinene, *cis*-pinonic acid, pinic acid, and pinonaldehyde in samples from a Finnish forest site (in logarithmic scale). Note that the sampling was done only during the daytime, and thus the trendlines are based on daytime values only.

concentrations were slightly overestimated, the concentration trends were clear (Fig. 4).

It is important to keep the sampling time to a minimum in order to understand the behavior of organic species during the day and their contribution to aerosol formation and growth. Fortunately, two particle formation events took place during the sampling period (27 and 28 April 2007, Julian dates 117 and 118), and a few differences in concentrations of the compounds were noticed between event and non-event days. Pinonaldehyde concentration decreased consistently from morning to afternoon during the first event day, probably due to its oxidation to corresponding acid. During non-event days, the concentration increased until about noon and decreased in the afternoon. The reason for this pattern is not yet clear. Pinic acid followed approximately the same trend as pinonaldehyde. Its decreasing concentration during the particle formation events can most probably be explained by the formation of dimers or by its oxidation. During the new particle formation days, *cis*-pinonic acid behaved like pinic acid, whereas during the non-event days it behaved uniquely.

The concentration maximum tended to appear later in the day presumably due to the different formation mechanism, while α -pinene concentration decreased sharply during the first event day, due to oxidation by UV light and ozone. For practical reasons, PILS samples could not, unfortunately, be collected during the night.

The advantage of coupling PILS with atmospheric pressure MS is the soft ionization which produces more information about molecular ions in aerosol species and in MSⁿ spectra than does the electron impact ionization used in commercial aerosol mass spectrometers. We collected PILS samples and introduced them, with no extra treatment except the addition of 5% of acetonitrile, to the electrospray ionization ion trap mass spectrometer (Fig. 5). Acetonitrile improved the ionization process. Two ions, belonging presumably to pinic and *cis*-pinonic acids, were identified in the MS/MS spectra (Fig. 5). As would be expected, a water molecule and a carbon dioxide molecule from the carboxyl group are lost from both acids. However, there are many acids with masses of 185 and 183, which could give exactly the same MS/MS spectra, but since the samples

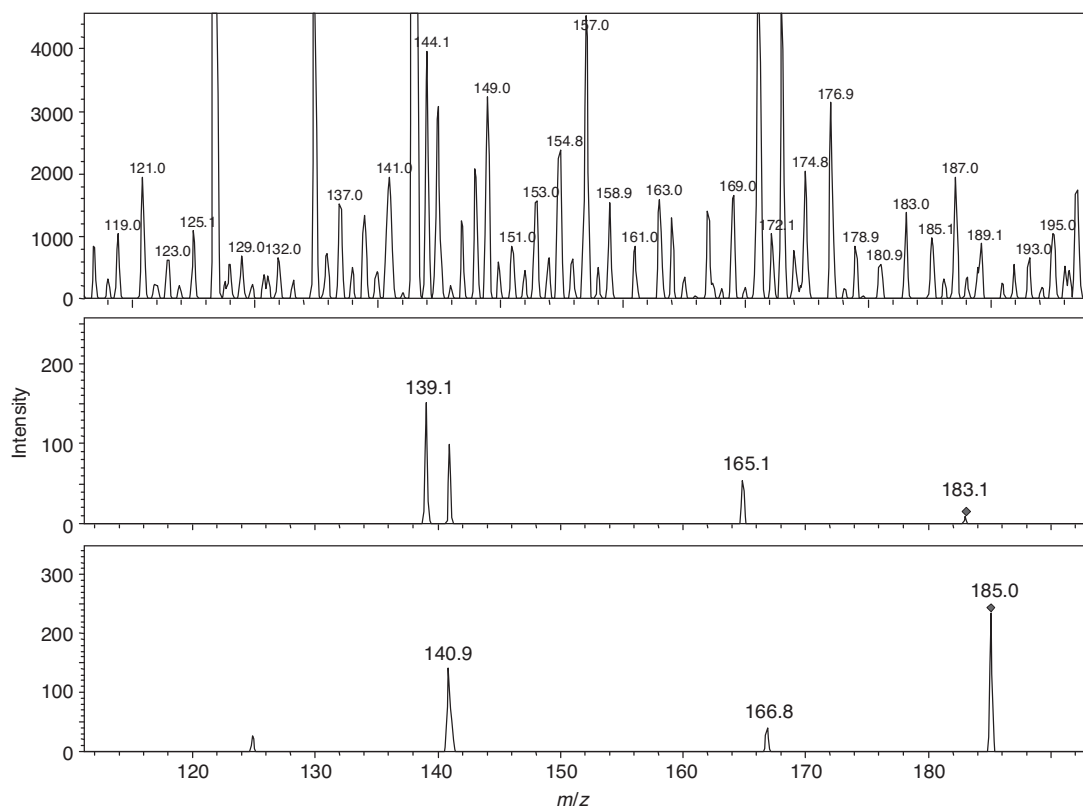


Fig. 5. ESI mass spectra for a directly injected PILS sample (top panel: 25 August 2007, from 12:00 to 13:00) and MS/MS spectra from ions 183 (middle panel) and 185 (bottom panel). See text for more information.

were collected in a Finnish Scots pine forest, the probability is high that the ions are from pinic and *cis*-pinonic acids. This is also confirmed by the GC-MS analysis. The PILS together with the ESI-MS is a promising instrumental combination for the determination of the compounds of interest in aerosol particles. The drawback that exact concentrations cannot be reliably determined, owing to differences in ionization and aerosol pH and salt composition of the samples, could be overcome by adding a reference compound, through the T-piece, to the PILS sample line.

Conclusions

For the first time, α -pinene and its oxidation products were collected from atmospheric aerosols with the particle-into-liquid sampler. The sampling set up, including coated denuders, transport flow solvent, collection time and

the final analysis step, were optimized for the selected compounds. The PILS proved to be a suitable sampling technique for the elucidation of organic compounds in atmospheric aerosols with good time resolution. Minimized oxidation, removal of gas-phase compounds, liquid sample flow, and on-line coupling without sample pre-treatment are benefits that overcome the few disadvantages, such as high tip temperature, low sample air flow, and the need to use water as transport flow solvent.

Acknowledgments: Financial support was provided by the Academy of Finland Centre of Excellence program (project no. 111 8615) and Helsinki University Environmental Research Center (HERC). We would like to thank Sari Järvinmäki for helping in the laboratory and Pasi Aalto from the Department of Physics for the instrument arrangements at Hyytiälä station. We are grateful to Heikki Junninen for providing the meteorological data and to prof. Risto Hillamo from the Finnish Meteorological Institute for invaluable comments.

References

- Allan J.D., Alfarra M.R., Bower K.N., Coe H., Jayne J.T., Worsnop D.R., Aalto P.P., Kulmala M., Hyötyläinen T., Cavalli F. & Laaksonen A. 2006. Size and composition measurements of background aerosol and new particle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer. *Atmos. Chem. Phys.* 6: 315–327.
- Drewnick F., Hings S.S., DeCarlo P., Jayne J.T., Gonin M., Fuhrer K., Weimer S., Jimenez J.L., Demerjian K.L., Borrmann S. & Worsnop D.R. 2005. A new time-of-flight aerosol mass spectrometer (TOF-AMS): instrument description and first field deployment. *Aerosol Sci. Technol.* 39: 637–658.
- Glasius M., Calogirou A., Jensen N.R., Hjorth J. & Nielsen C.J. 1997. Kinetic study of gas-phase reactions of pinonaldehyde and structurally related compounds. *Int. J. Chem. Kinet.* 29: 527–533.
- Handbook of Chemistry and Physics* (67th ed.) 1986–1987. CRC Press Inc., Boca Raton, USA.
- Helmig D. & Greenberg J. 1995. Artifact formation from the use of potassium-iodide-based ozone traps during atmospheric sampling of trace organic gases. *J. High Res. Chrom.* 18: 15–18.
- Jaoui M. & Kamens R.M. 2001. Mass balance of gaseous and particulate products analysis from α -pinene/ NO_3 /air in the presence of natural sunlight. *J. Geophys. Res.* 106: 12541–12558.
- Kondo Y., Miyazaki Y., Takegawa N., Miyakawa T., Weber R.J., Jimenez J.L., Zhang Q. & Worsnop D.R. 2007. Oxygenated and water-soluble organic aerosols in Tokyo. *J. Geophys. Res.* 112, D01203, doi:10.1029/2006JD007056.
- Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Boy M., Lauri A., Kerminen V.-M., Birmili W. & McMurry P.H. 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol. Sci.* 35: 143–176.
- Kulmala M., Hämeri K., Aalto P.P., Mäkelä J., Pirjola L., Nilsson E.D., Buzorius G., Rannik U., Dal Maso M., Seidl W., Hoffmann T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.
- Liggio J. & Li S.-M. 2006. Reactive uptake of pinonaldehyde on acidic aerosols. *J. Geophys. Res.* 111, D24303, doi: 10.1029/2005JD006978.
- Liu Y., Sklorz M., Schnelle-Kreis J., Orasche J., Ferge T., Kettrup A. & Zimmermann R. 2006. Oxidant denuder sampling for analysis of polycyclic aromatic hydrocarbons and their oxygenated derivatives in ambient aerosol: evaluation of sampling artifact. *Chemosphere* 62: 1889–1898.
- Lohmann U. & Feichter J. 2005. Global indirect aerosol effects: a review. *Atmos. Chem. Phys.* 5: 715–737.
- Mader B. & Pankow J.F. 2001. Gas/solid partitioning of semi-volatile organic compounds (SOCs) to air filters. 3. An analysis of gas adsorption artifacts in measurement of atmospheric SOC and organic carbon (OC) when using Teflon membrane filters and quartz fiber filters. *Environ. Sci. Technol.* 35: 3422–3432.
- Orsini D.A., Ma Y., Sullivan A., Sierau B., Baumann K. & Weber R.J. 2003. Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. *Atmos. Environ.* 37: 1243–1259.
- Parshintsev J., Nurmi J., Kilpeläinen I., Hartonen K., Kulmala M. & Riekkola M.-L. 2008. Preparation of β -caryophyllene oxidation products and their determination in ambient aerosol samples. *Anal. Bioanal. Chem.* 390: 913–919.
- Rissanen T., Hyötyläinen T., Kallio M., Kronholm J., Kulmala M. & Riekkola M.-L. 2006. Characterization of organic compounds in aerosol particles from a coniferous forest by GC-MS. *Chemosphere* 64: 1185–1195.
- Sillanpää M., Hillamo R., Saarikoski S., Frey A., Pennanen A., Makkonen U., Spolnik Z., Van Grieken R., Branis M., Brunekreef B., Chalbot M.-C., Kuhlbusch T., Sunyer J., Kerminen V.-M., Kulmala M. & Salonen R. 2006. Chemical composition and mass closure of particulate matter at six urban sites in Europe. *Atmos. Environ.* 40: 212–223.
- Spracklen D.V., Carslaw K.S., Kulmala M., Kerminen V.-M., Mann G.W. & Sihto S.-L. 2006. The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales. *Atmos. Chem. Phys.* 6: 5631–5648.
- Sullivan A.P., Peltier R.E., Brock C.A., de Gouw J.A., Holloway J.S., Warneke C., Wollny A.G. & Weber R.J. 2006. Airborne measurement of carbonaceous aerosol soluble in water over northeastern United States: method development and an investigation into water-soluble organic carbon sources. *J. Geophys. Res.* 111, D23S46, doi:10.1029/2006JD007072.
- Viidanoja J., Kerminen V.-M. & Hillamo R. 2002. Measuring the size distribution of atmospheric organic and black carbon using impactor sampling coupled with thermal carbon analysis: method development and uncertainties. *Aerosol Sci. Technol.* 36: 607–616.
- Warnke J., Bandur R. & Hoffmann T. 2006. Capillary-HPLC-ESI-MS/MS method for the determination of acidic products from the oxidation of monoterpenes in atmospheric aerosol samples. *Anal. Bioanal. Chem.* 385: 34–45.
- Weber R.J., Orsini D., Daun Y., Lee Y.-N., Klotz P.J. & Brechtel F. 2001. A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol Sci. Technol.* 35: 718–727.
- Williams E.L. & Grosjean D. 1990. Removal of atmospheric oxidants with annular denuders. *Environ. Sci. Technol.* 24: 811–814.